A

Practitioner's Docket No. 50351 ***PATENT***

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Box Patent Application
Assistant Commissioner for Patents
Washington, D.C. 20231

NEW APPLICATION TRANSMITTAL

Transmitted herewith for filing is the patent application of

Inventor(s): **Peter Trefonas, III**
Gary N. Taylor

WARNING: *37 C.F.R. § 1.41(a)(1) points out*

"(a) A patent is applied for in the name or names of the actual inventor or inventors.

"(1) The inventorship of a nonprovisional application is that inventorship set forth in the oath or declaration as prescribed by § 1.63, except as provided for in § 1.53(d)(4) and § 1.63(d). If an oath or declaration as prescribed by § 1.63 is not filed during the pendency of a nonprovisional application, the inventorship is that inventorship set forth in the application papers filed pursuant to § 1.53(b), unless a petition under this paragraph accompanied by the fee set forth in § 1.17(i) is filed supplying or changing the name or names of the inventor or inventors."

For (title): **PHOTORESIST COMPOSITIONS PARTICULARLY SUITABLE FOR SHORT WAVELENGTH IMAGING**

CERTIFICATION UNDER 37 C.F.R. 1.10*
*(Express Mail label number is **mandatory**.)*
(Express Mail certification is optional.)

I hereby certify that this New Application Transmittal and the documents referred to as attached therein are being deposited with the United States Postal Service on this date 12/23/98, in an envelope as "Express Mail Post Office to Addressee," mailing Label Number EL117825509US, addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231

Deanna M. Landry
(type or print name of person mailing paper)

Deanna M. Landry
Signature of person mailing paper

WARNING: *Certificate of mailing (first class) or facsimile transmission procedures of 37 C.F.R. 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence*

****WARNING:*** *Each paper or fee filed by "Express Mail" **must** have the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 C.F.R. 1.10(b)*
*"Since the filing of correspondence under § 1.10 without the Express Mail mailing label thereon is an oversight that can be avoided by the exercise of reasonable care, requests for waiver of this requirement will **not** be granted on petition." Notice of Oct. 24, 1996, 60 Fed. Reg. 56,439, at 56,442*

1. Type of Application

This new application is for a(n)

(check one applicable item below)

☒ Original (nonprovisional)

☐ Design

☐ Plant

WARNING: ***Do not*** *use this transmittal for a completion in the U S of an International Application under 35 U.S.C. 371(c)(4), unless the International Application is being filed as a divisional, continuation or continuation-in-part application*

WARNING: ***Do not*** *use this transmittal for the filing of a provisional application*

NOTE If one of the following 3 items apply, then complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF A PRIOR U S APPLICATION CLAIMED and a NOTIFICATION IN PARENT APPLICATION OF THE FILING OF THIS CONTINUATION APPLICATION

☐ Divisional.

☐ Continuation.

☐ Continuation-in-part (C-I-P)

2. Benefit of Prior U.S. Application(s) (35 U.S.C. 119(e), 120, or 121)

NOTE A nonprovisional application may claim an invention disclosed in one or more prior filed copending nonprovisional applications or copending international applications designating the United States of America. In order for a nonprovisional application to claim the benefit of a prior filed copending nonprovisional application or copending international application designating the United States of America, each prior application must name as an inventor at least one inventor named in the later filed nonprovisional application and disclose the named inventor's invention claimed in at least one claim of the later filed nonprovisional application in the manner provided by the first paragraph of 35 U S C 112 Each prior application must also be

(i) An international application entitled to a filing date in accordance with PCT Article 11 and designating the United States of America, or

(ii) Complete as set forth in § 1 51(b), or

(iii) Entitled to a filing date as set forth in § 1 53(b) or § 1 53(d) and include the basic filing fee set forth in § 1 16, or

(iv) Entitled to a filing date as set forth in § 1 53(b) and have paid therein the processing and retention fee set forth in § 1 21(l) within the time period set forth in § 1 53(f)

37 C F R § 1 78(a)(1)

NOTE If the new application being transmitted is a divisional, continuation or a continuation-in-part of a parent case, or where the parent case is an International Application which designated the U.S , or benefit of a prior provisional application is claimed, then check the following item and complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U S. APPLICATION(S) CLAIMED.

WARNING: *If an application claims the benefit of the filing date of an earlier filed application under 35 U.S.C. 120, 121 or 365(c), the 20–year term of that application will be based upon the filing date of the earliest U.S application that the application makes reference to under 35 U.S C 120, 121 or 365(c) (35 U S C. 154(a)(2) does not take into account, for the determination of the patent term, any application on which priority is claimed under 35 U S C 119, 365(a) or 365(b).) For a c–i–p application, applicant should review whether any claim in the patent that will issue is supported by an earlier application and, if not, the applicant should consider canceling the reference to the earlier filed application The term of a patent is not based on a claim-by-claim approach. See Notice of April 14, 1995, 60 Fed Reg 20,195, at 20,205*

WARNING: *When the last day of pendency of a provisional application falls on a Saturday, Sunday, or Federal holiday within the District of Columbia, any nonprovisional application claiming benefit of the provisional application* ***must*** *be filed prior to the Saturday, Sunday, or Federal holiday within the District of Columbia See 37 C F R § 1 78(a)(3)*

☐ The new application being transmitted claims the benefit of prior U.S. application(s). Enclosed are ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U S. APPLICATION(S) CLAIMED.

3. Papers Enclosed

A. Required for filing date under 37 C.F R § 1.53(b) (Regular) or 37 C.F.R. § 1.153 (Design) Application

22 Pages of specification

4 Pages of claims

____ Sheets of drawing

WARNING: ***DO NOT*** *submit original drawings A high quality copy of the drawings should be supplied when filing a patent application The drawings that are submitted to the Office must be on strong, white, smooth, and non-shiny paper and meet the standards according to § 1 84. If corrections to the drawings are necessary, they should be made to the original drawing and a high-quality copy of the corrected original drawing then submitted to the Office Only one copy is required or desired For comments on proposed then-new 37 CFR 1 84, see Notice of March 9, 1988 (1990 O.G. 57-62).*

NOTE "Identifying indicia, if provided, should include the application number or the title of the invention, inventor's name, docket number (if any), and the name and telephone number of a person to call if the Office is unable to match the drawings to the proper application This information should be placed on the back of each sheet of drawing a minimum distance of 1 5 cm (5/8 inch) down from the top of the page . . ." 37 C F.R 1 84(c))

(complete the following, if applicable)

☐ The enclosed drawing(s) are photograph(s), and there is also attached a "PETITION TO ACCEPT PHOTOGRAPH(S) AS DRAWING(S)." 37 C.F.R. 1.84(b).

☐ formal

☐ informal

B. Other Papers Enclosed

____ Pages of declaration and power of attorney

1 Pages of abstract

____ Other

4. Additional papers enclosed

☐ Amendment to claims

☐ Cancel in this applications claims _____ before calculating the filing fee. (At least one original independent claim must be retained for filing purposes)

☐ Add the claims shown on the attached amendment. (Claims added have been numbered consecutively following the highest numbered original claims.)

☐ Preliminary Amendment

☐ Information Disclosure Statement (37 C.F R. 1.98)

☐ Form PTO–1449 (PTO/SB/08A and 08B)

☐ Citations

☐ Declaration of Biological Deposit

☐ Submission of "Sequence Listing," computer readable copy and/or amendment pertaining thereto for biotechnology invention containing nucleotide and/or amino acid sequence.

☐ Authorization of Attorney(s) to Accept and Follow Instructions from Representative

☐ Special Comments

☐ Other

5. Declaration or oath (including power of attorney)

NOTE A newly executed declaration is not required in a continuation or divisional application provided that the prior nonprovisional application contained a declaration as required, the application being filed is by all or fewer than all the inventors named in the prior application, there is no new matter in the application being filed, and a copy of the executed declaration filed in the prior application (showing the signature or an indication thereon that it was signed) is submitted. The copy must be accompanied by a statement requesting deletion of the names of person(s) who are not inventors of the application being filed. If the declaration in the prior application was filed under § 1.47, then a copy of that declaration must be filed accompanied by a copy of the decision granting § 1.47 status or, if a nonsigning person under § 1.47 has subsequently joined in a prior application, then a copy of the subsequently executed declaration must be filed. See 37 C.F.R. §§ 1.63(d)(1)–(3).

NOTE A declaration filed to complete an application must be executed, identify the specification to which it is directed, identify each inventor by full name including family name and at least one given name, without abbreviation together with any other given name or initial, and the residence, post office address and country or citizenship of each inventor, and state whether the inventor is a sole or joint inventor. 37 C.F.R. § 1.63(a)(1)–(4).

☒ Enclosed

Executed by

(check **all** *applicable boxes)*

☒ inventor(s).

☐ legal representative of inventor(s). 37 CFR 1.42 or 1.43.

☐ joint inventor or person showing a proprietary interest on behalf of inventor who refused to sign or cannot be reached.

☐ This is the petition required by 37 CFR 1.47 and the statement required by 37 CFR 1.47 is also attached. *See* item 13 below for fee.

☐ Not Enclosed.

NOTE Where the filing is a completion in the U.S. of an International Application or where the completion of the U.S. application contains subject matter in addition to the International Application, the application may be treated as a continuation or continuation-in-part, as the case may be, utilizing ADDED PAGE FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION CLAIMED.

☐ Application is made by a person authorized under 37 C.F.R. 1.41(c) on behalf of *all* the above named inventor(s).

(The declaration or oath, along with the surcharge required by 37 CFR 1.16(e) can be filed subsequently)

☐ Showing that the filing is authorized *(not required unless called into question 37 CFR 1.41(d))*

6. Inventorship Statement

WARNING: *If the named inventors are each not the inventors of all the claims an explanation, including the ownership of the various claims at the time the last claimed invention was made, should be submitted*

The inventorship for all the claims in this application are:

☒ The same.

or

☐ Not the same. An explanation, including the ownership of the various claims at the time the last claimed invention was made,

☐ is submitted.

☐ will be submitted.

7. Language

NOTE An application including a signed oath or declaration may be filed in a language other than English An English translation of the non-English language application and the processing fee of $130 00 required by 37 CFR 1.17(k) is required to be filed with the application, or within such time as may be set by the Office 37 CFR 1 52(d).

☒ English

☐ Non-English

☐ The attached translation includes a statement that the translation is accurate. 37 C.F.R. 1.52(d).

8. Assignment

☒ An assignment of the invention to **Shipley Company, L.L.C. of Marlborough, Massachusetts, U.S.A. 01752**

☒ is attached. A separate ☐ "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or ☒ FORM PTO 1595 is also attached.

☐ will follow.

NOTE "If an assignment is submitted with a new application, send two separate letters-one for the application and one for the assignment " Notice of May 4, 1990 (1114 O G 77-78)

WARNING: *A newly executed "CERTIFICATE UNDER 37 CFR 3 73(b)" must be filed when a continuation-in-part application is filed by an assignee Notice of April 30, 1993, 1150 O G 62-64*

9. Certified Copy

Certified copy(ies) of application(s)

Country	Appln No	Filed
Country	Appln No.	Filed
Country	Appln. No	Filed

from which priority is claimed

☐ is (are) attached.

☐ will follow.

NOTE The foreign application forming the basis for the claim for priority must be referred to in the oath or declaration 37 CFR 1.55(a) and 1.63

NOTE This item is for any foreign priority for which the application being filed directly relates. If any parent U.S. application or International Application from which this application claims benefit under 35 U.S.C. 120 is itself entitled to priority from a prior foreign application, then complete item 18 on the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED

10. Fee Calculation (37 C.F.R. 1.16)

A. ☒ Regular application

CLAIMS AS FILED				
Number filed	Number Extra		Rate	Basic Fee 37 C.F.R. 1.16(a)
				~~$790.00~~ **760.00**
Total Claims (37 CFR 1.16(c)) **21** – 20 =	**1**	×	$ 22.00	**18.00**
Independent Claims (37 CFR 1.16(b)) **3** – 3 =		×	$ 82.00	
Multiple dependent claim(s), if any (37 CFR 1.16(d))		+	$270.00	

☐ Amendment cancelling extra claims is enclosed.

☐ Amendment deleting multiple-dependencies is enclosed.

☐ Fee for extra claims is not being paid at this time.

NOTE If the fees for extra claims are not paid on filing they must be paid or the claims cancelled by amendment, prior to the expiration of the time period set for response by the Patent and Trademark Office in any notice of fee deficiency 37 CFR 1.16(d)

Filing Fee Calculation $ **778.00**

B. ☐ Design application ($330.00—37 CFR 1.16(f))

Filing Fee Calculation $_____

C. ☐ Plant application ($540.00—37 CFR 1.16(g))

Filing fee calculation $_____

11. Small Entity Statement(s)

☐ Statement(s) that this is a filing by a small entity under 37 CFR 1.9 and 1.27 is (are) attached

WARNING: *"Status as a small entity must be specifically established in each application or patent in which the status is available and desired. Status as a small entity in one application or patent does not affect any other application or patent, including applications or patents which are directly or indirectly dependent upon the application or patent in which the status has been established. The refiling of an application under § 1.53 as a continuation, division, or continuation-in-part (including a continued prosecution application under § 1.53(d)), or the filing of a reissue application requires a new determination as to continued entitlement to small entity status for the continuing or reissue application. A nonprovisional application claiming benefit under 35 U.S.C. 119(e), 120, 121, or 365(c) of a prior application, or a reissue application may rely on a statement filed in the prior application or in the patent if the nonprovisional application or the reissue application includes a reference to the statement in the prior application or in the patent or includes a copy of the statement in the prior application or in the patent and status as a small entity is still proper and desired. The payment of the small entity basic statutory filing fee will be treated as such a reference for purposes of this section." 37 C.F.R. § 1.28(a)(2)*

(complete the following, if applicable)

☐ Status as a small entity was claimed in prior application

_____ / _____, filed on _____, from which benefit is being claimed for this application under:

35 U.S.C. ☐ 119(e),
☐ 120,
☐ 121,
☐ 365(c),

and which status as a small entity is still proper and desired

☐ A copy of the statement in the prior application is included

Filing Fee Calculation (50% of **A**, **B** or **C** above)

$_____

NOTE *Any excess of the full fee paid will be refunded if small entity status is established and a refund request are filed within 2 months of the date of timely payment of a full fee. The two-month period is not extendable under § 1.136. 37 CFR 1.28(a)*

12. Request for International-Type Search (37 C.F.R. 1.104(d))

(complete, if applicable)

☐ Please prepare an international-type search report for this application at the time when national examination on the merits takes place

13. Fee Payment Being Made at This Time

☐ Not Enclosed

☐ No filing fee is to be paid at this time.
(This and the surcharge required by 37 C.F.R. 1.16(e) can be paid subsequently.)

☒ Enclosed

☒ Filing fee	$ 778.00
☒ Recording assignment ($40.00; 37 C.F.R. 1.21(h)) (See attached "COVER SHEET FOR ASSIGNMENT ACCOMPANYING NEW APPLICATION")	$ 40.00
☐ Petition fee for filing by other than all the inventors or person on behalf of the inventor where inventor refused to sign or cannot be reached ($130.00; 37 C F R. 1.47 and 1.17(i))	$ _____
☐ For processing an application with a specification in a non-English language ($130.00; 37 C F R. 1.52(d) and 1.17(k))	$ _____
☐ Processing and retention fee ($130.00; 37 C F R 1 53(d) and 1 21(l))	$ _____
☐ Fee for international-type search report ($40.00; 37 C.F.R. 1 21(e))	$ _____

NOTE: 37 CFR 1.21(l) establishes a fee for processing and retaining any application that is abandoned for failing to complete the application pursuant to 37 CFR 1.53(f) and this, as well as the changes to 37 CFR 1 53 and 1.78(a)(1), indicate that in order to obtain the benefit of a prior U.S. application, either the basic filing fee must be paid, or the processing and retention fee of § 1 21(l) must be paid, within 1 year from notification under § 53(f)

Total fees enclosed $ 818.00

14. Method of Payment of Fees

☒ Check in the amount of $ 818.00

☐ Charge Account No _____ in the amount of $_____.

A duplicate of this transmittal is attached.

NOTE: Fees should be itemized in such a manner that it is clear for which purpose the fees are paid 37 CFR 1 22(b).

15. Authorization to Charge Additional Fees

WARNING: *If no fees are to be paid on filing, the following items should not be completed.*

WARNING: *Accurately count claims, especially multiple dependent claims, to avoid unexpected high charges, if extra claim charges are authorized.*

☒ The Commissioner is hereby authorized to charge the following additional fees by this paper and during the entire pendency of this application to Account No. 04-1105 :

- ☒ 37 C.F.R. 1.16(a), (f) or (g) (filing fees)
- ☐ 37 C.F.R. 1.16(b), (c) and (d) (presentation of extra claims)

NOTE: Because additional fees for excess or multiple dependent claims not paid on filing or on later presentation must only be paid or these claims cancelled by amendment prior to the expiration of the time period set for response by the PTO in any notice of fee deficiency (37 CFR 1.16(d)), it might be best not to authorize the PTO to charge additional claim fees, except possibly when dealing with amendments after final action.

- ☐ 37 C.F.R. 1.16(e) (surcharge for filing the basic filing fee and/or declaration on a date later than the filing date of the application)
- ☐ 37 C.F.R. §§ 1.17(a)(1)–(5) (extension fees pursuant to § 1.136(a)).
- ☒ 37 C.F.R. 1.17 (application processing fees)

NOTE: ". . .A written request may be submitted in an application that is an authorization to treat any concurrent or future reply, requiring a petition for an extension of time under this paragraph for its timely submission, as incorporating a petition for extension of time for the appropriate length of time. An authorization to charge all required fees, fees under § 1.17, or all required extension of time fees will be treated as a constructive petition for an extension of time in any concurrent or future reply requiring a petition for an extension of time under this paragraph for its timely submission. Submission of the fee set forth in § 1.17(a) will also be treated as a constructive petition for an extension of time in any concurrent reply requiring a petition for an extension of time under this paragraph for its timely submission." 37 C.F.R. § 1.136(a)(3).

- ☐ 37 C.F.R. 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 C.F.R. 1.311(b))

NOTE: Where an authorization to charge the issue fee to a deposit account has been filed before the mailing of a Notice of Allowance, the issue fee will be automatically charged to the deposit account at the time of mailing the notice of allowance. 37 CFR 1.311(b).

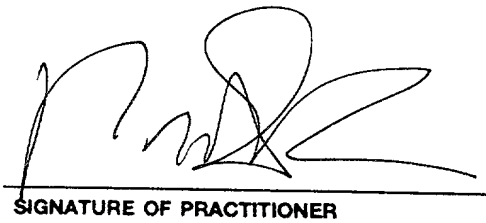
NOTE: 37 CFR 1.28(b) requires "Notification of any change in status resulting in loss of entitlement to small entity status must be filed in the application . . . prior to paying, or at the time of paying, . . . the issue fee. . . ." From the wording of 37 CFR 1.28(b), (a) notification of change of status must be made even if the fee is paid as "other than a small entity" and (b) no notification is required if the change is to another small entity.

16. Instructions as to Overpayment

NOTE: ". . . Amounts of twenty-five dollars or less will not be returned unless specifically requested within a reasonable time, nor will the payer be notified of such amounts; amounts over twenty-five dollars may be returned by check or, if requested, by credit to a deposit account." 37 C.F.R. § 1.26(a).

☒ Credit Account No. 04-1105

☐ Refund



SIGNATURE OF PRACTITIONER

Reg. No. 33,860

Peter F. Corless

(type or print name of attorney)

Tel. No. (508) 485-7772

P.O. Box 556

P.O. Address

Customer No.

Marlborough, MA 01752

☒ **Incorporation by reference of added pages**

(check the following item if the application in this transmittal claims the benefit of prior U.S. application(s) (including an international application entering the U.S. stage as a continuation, divisional or C-I-P application) and complete and attach the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED)

☐ Plus Added Pages for New Application Transmittal Where Benefit of Prior U.S. Application(s) Claimed

Number of pages added _____

☐ Plus Added Pages for Papers Referred to in Item 4 Above

Number of pages added _____

☐ Plus added pages deleting names of inventor(s) named in prior application(s) who is/are no longer inventor(s) of the subject matter claimed in this application.

Number of pages added _____

☒ Plus "Assignment Cover Letter Accompanying New Application"

Number of pages added 3

☐ **Statement Where No Further Pages Added**

(if no further pages form a part of this Transmittal, then end this Transmittal with this page and check the following item)

☐ This transmittal ends with this page.

Docket No. 50351
Express Mail Label No. EL117825509US

PHOTORESIST COMPOSITIONS PARTICULARLY SUITABLE FOR SHORT WAVELENGTH IMAGING

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to new photoresist compositions, particularly chemically-amplified positive-acting resists that can be imaged at extremely short wavelengths such as 193 nm.

2. Background

Photoresists are photosensitive films used for transfer of images to a substrate. A coating layer of a photoresist is formed on a substrate and the photoresist layer is then exposed through a photomask to a source of activating radiation. The photomask has areas that are opaque to activating radiation and other areas that are transparent to activating radiation. Exposure to activating radiation provides a photoinduced chemical transformation of the photoresist coating to thereby transfer the pattern of the photomask to the photoresist-coated substrate. Following exposure, the photoresist is developed to provide a relief image that permits selective processing of a substrate.

A photoresist can be either positive-acting or negative-acting. For most negative-acting photoresists, those coating layer portions that are exposed to activating radiation polymerize or crosslink in a reaction between a photoactive compound and polymerizable reagents of the photoresist composition. Consequently, the exposed coating portions are rendered less soluble in a developer solution than unexposed portions. For a positive-acting photoresist, exposed portions are rendered more soluble in a developer solution while areas not exposed remain comparatively less developer soluble.

In general, photoresist compositions comprise at least a resin binder component and a photoactive agent. Photoresist compositions are described in Deforest, *Photoresist*

Materials and Processes, McGraw Hill Book Company, New York, ch. 2, 1975 and by Moreau, *Semiconductor Lithography, Principles, Practices and Materials*, Plenum Press, New York, ch. 2 and 4, both incorporated herein by reference for their teaching of photoresist compositions and methods of making and using the same.

More recently, chemically-amplified-type resists have been increasingly employed, particularly for formation of sub-micron images and other high performance applications. Such photoresists may be negative-acting or positive-acting and generally include many crosslinking events (in the case of a negative-acting resist) or deprotection reactions (in the case of a positive-acting resist) per unit of photogenerated acid. In the case of positive chemically-amplified resists, certain cationic photoinitiators have been used to induce cleavage of certain "blocking" groups pendant from a photoresist binder, or cleavage of certain groups that comprise a photoresist binder backbone. See, for example, U.S. Patents Nos. 5,075,199; 4,968,581; 4,883,740; 4,810,613; and 4,491,628, and Canadian Patent Application 2,001,384. Upon cleavage of the blocking group through exposure of a coating layer of such a resist, a polar functional group is formed, e.g., carboxyl or imide, which results in different solubility characteristics in exposed and unexposed areas of the resist coating layer.

While currently available photoresists are suitable for many applications, current resists also can exhibit significant shortcomings, particularly in high performance applications such as formation of highly resolved sub-half micron and sub-quarter micron features.

In this regard, photoresists that could be successfully imaged at extremely short wavelengths such as 193 nm (provided by an ArF exposure tool) would be highly desirable. Use of such short exposure wavelengths can enable formation of smaller features. Accordingly, a photoresist that yields well-resolved images upon 193 nm exposure could enable formation of extremely small (e.g. sub-0.25 μm) features that

respond to constant industry demands for smaller dimension circuit patterns, e.g. to provide greater circuit density and enhanced device performance.

However, current photoresists are generally designed for imaging at relatively higher wavelengths, such as I-line (365 nm) and G-line (436 nm) exposures. Even advanced resist products, such as those imaged with a KrF laser (ca. 248 nm), utilize exposure wavelengths that are substantially higher than 193 nm.

Such current photoresists are generally unsuitable for imaging at 193 nm. In particular, prior resists exhibit poor resolution (if any image at all can be developed) upon exposure to 193 nm. Among other things, current photoresists can be highly opaque to extremely short exposure wavelengths such as 193 nm, thereby resulting in poorly resolved images. Efforts to enhance transparency at 193 nm can result in resists can compromise other lithographic properties such as substrate adhesion, which in turn can dramatically compromise image resolution.

It thus would be desirable to have new photoresist compositions, particularly resist compositions that can be imaged at 193 nm.

SUMMARY OF THE INVENTION

The present invention provides new photoresist compositions, including resists that can be effectively imaged at extremely short wavelengths such as 193 nm. Preferred resists of the invention are chemically-amplified positive-acting resists that contain an added amine.

More particularly, in a first aspect, the resists of the invention in general comprise a resin, a photoacid generator and an added amine component. The amine preferably is 1) non-aromatic, 2) has from about 7 to about 20 carbon atoms, more preferably from about 9 to about 16 carbon atoms, and/or 3) contains no primary or secondary amine

groups. It is further preferred that the amine contains no multiple tertiary amine groups where two tertiary groups are separated by a linkage of optionally substituted $-CH_2CH_2-$ (i.e. optionally substituted ethylene). The terms primary, secondary and tertiary amine groups are used herein in accordance with well-recognized meaning, i.e. a primary amine has two hydrogen substituents and one non-hydrogen substituent; a secondary amine has one hydrogen substituent and two non-hydrogen substituents; and a tertiary amine has three non-hydrogen substituents.

We have found that photoresists that contain such an amine additive exhibit surprisingly enhanced lithographic results, particularly upon imaging at short exposure wavelengths such as sub-200 nm wavelengths, particularly 193 nm. See, for instance, the results set forth in the examples which follow.

In a related aspect, the amine component of a resist of the invention is a "hindered amine" which is a non-aromatic amine that comprises either 1) a tertiary nitrogen alicyclic ring member, and preferably is at junction position between a bicyclic or other multi-ring ring system; or 2) a tertiary nitrogen that is not a ring member, and is substituted by at least two secondary or tertiary carbon radicals, preferably two tertiary carbon radicals such as tert-butyl and the like. Thus, exemplary preferred hindered amines of group 1) include diazabicycloundecene and diazabicyclononene. A preferred hindered amine of group 2) is di-tert-butylethanolamine. References herein to a "tertiary" carbon radical indicate the carbon radical has two non-hydrogen substituents (i.e. $-\underline{C}HRR^1$ where R and R^1 are the same or different and each is other than hydrogen); and references herein to a "quaternary" carbon radical indicate the carbon radical has three non-hydrogen substituents (i.e. $-\underline{C}RR^1R^2$ where R, R^1 and R^2 are each the same or different and each is other than hydrogen). See, for instance, Morrison and Boyd, *Organic Chemistry*, particularly at page 85 (3rd ed., Allyn and Bacon), for a discussion of those terms secondary and tertiary.

Other amines are significantly less suitable for use in photoresists of the invention and therefore are excluded from the invention. In particular, we have found that use of non-cyclic amines that do not contain multiple substitution of tertiary or quarternary carbon radicals can result in delamination and cracking of a resist coating layer. For example, trioctyl amine, dimethylaminopyridine and ammonium compounds all can cause cracking of a resist coating layer. See, for instance, the results set forth in the examples which follow.

While a wide variety of photoacid generators (PAGs) may be suitably employed in photoresists of the invention, preferred PAGs for use in resists of the invention are non-ionic compounds. Suitable non-ionic PAGs include e.g. imidosulfonates, sulfonate esters, halogenated compounds that generate a halo-acid (e.g. HBr) upon photoactivation, and the like. As referred to herein, the term non-ionic photoacid generator is used in accordance with its art-recognized meaning, i.e. a non-ionic PAG does not have any ionic bonds, but rather typically has all covalent-type bonds. See, for example, Morrison and Boyd, *Organic Chemistry*, pages 3-5 (3rd ed., 1981).

The photoresist compositions of the invention can provide highly resolved relief images upon exposure to extremely short wavelengths, particularly 193 nm. The photoresists of the invention preferably are chemically-amplified positive resists, which utilize photoacid-induced cleavage of pendant polymer groups of the resin binder to provide solubility differentials between exposed and unexposed areas of a resist coating layer.

Preferred deblocking polymers for use as a resin binder component of resists of the invention include acrylate resins that have pendant ester groups that can react to provide polar acid groups in the presence of photogenerated acid.

Preferred polymers for use as a resist resin binder component in extremely short wavelength imaging applications (e.g. sub-200 nm imaging, particularly 193 nm) are substantially free of any phenyl or other aromatic groups. For example, preferred polymers contain less than about 1 mole percent aromatic groups, more preferably less than about 0.1, 0.02, 0.04 and 0.08 mole percent aromatic groups and still more preferably less than about 0.01 mole percent aromatic groups. Particularly preferred polymers are completely free of aromatic groups. Aromatic groups can be highly absorbing of sub-200 nm radiation and thus are undesirable for polymers used in photoresists of the invention.

Preferred resists of the invention exhibit suitable properties for imaging at 193 nm, including good adhesion (e.g., no visible (naked eye) delamination or cracking through development) to an underlying substrate surface, such as a silicon wafer or other microelectronic wafer surface, a glass or plastic flat panel display surface, an antireflective coating (ARC), etc. Preferred resists also exhibit good resolution upon development (e.g., vertical sidewalls, no feature swelling), even at sub-0.25 μm feature sizes.

The invention also provides methods for forming relief images, including methods for forming a highly resolved relief image such as a pattern of lines where each line has essentially vertical sidewalls and a line width of about 0.40 microns or less, and even a width of about 0.25 or 0.20 microns or less. The invention further provides articles of manufacture comprising substrates such as a microelectronic wafer substrate having coated thereon a polymer, photoresist or resist relief image of the invention.

Other aspects of the invention are disclosed infra.

DETAILED DESCRIPTION OF THE INVENTION

As stated above, photoresists of the invention are preferably chemically-amplified positive resists that in general comprise a resin binder, a photoacid generator (PAG) and an added amine.

In a first aspect, the added amine preferably 1) non-aromatic 2) has from about 7 to about 20 carbon atoms, more preferably from about 9 to about 16 carbon atoms, and/or 3) contains no primary or secondary amine groups. It is further preferred in this aspect that the added amine contains no multiple tertiary amine groups where two tertiary groups are separated by a linkage of optionally substituted $-CH_2CH_2-$ (i.e. optionally substituted ethylene).

In a related aspect, the added amine is a non-aromatic amine that comprises either 1) a tertiary nitrogen alicyclic ring member, and preferably is at junction position between a bicyclic or other multi-ring ring system; or 2) a tertiary nitrogen that is not a ring member, and is substituted by at least two tertiary or quaternary carbon radicals, preferably two quaternary carbon radicals. Hindered amines of type 1), i.e. that contain a tertiary nitrogen alicyclic ring members, preferably are bicyclic rings, rather than tricyclic or other multi-cyclic structures.

By stating that the amine is non-aromatic, it is meant that the compound contains an amine group that is not part of an aromatic ring, although the compound may be substituted with an aromatic substituent. Thus, for instance, with respect to the above-specified hindered amine additive, the tertiary nitrogen of 1) or 2) is not a ring member of an aromatic ring, although the compound may have an aromatic amine substituent. Preferably, however, the amine component of resists of the invention is free of any aromatic amine moieties, more preferably free of any aromatic moieties of any type.

An added amine of resists of the invention preferably is not excessively large. For example, preferably the total number of non-hydrogen atoms (e.g. C, N, O, etc.) of the hindered amine is about 40 or 35 or less, more preferably about 30 or less, still more preferably about 27, 26 or 25 or less total atoms other than hydrogen, yet more preferably about 24 total atoms other than hydrogens.

On the other hand, the added amine should be sufficiently non-volatile so it is not removed during a pre-exposure bake step of a resist formulation, where the carrier solvent is removed. Thus, preferably an added amine has at least about 5 or 6 non-hydrogen atoms, more preferably at least about 7 or 8 non-hydrogen atoms. Added amines having about 8, still more preferably about 9, 10 or 11 non-hydrogen atoms also will be preferred.

In general, a hindered added amine preferably will have from about 5 to about 35 or 40 non-hydrogen atoms, more typically from about 5 to about 30 non-hydrogen atoms. In many instances, preferred will be a hindered amine having from about 6 to about 25 non-hydrogen atoms, and even more preferred will be an added amine having from about 6 to about 24 non-hydrogen atoms. As discussed above, in the first aspect of the invention, the added amine preferably has from about 7 to about 20 carbon atoms, more preferably from about 9 to about 16 carbon atoms.

Specifically preferred added amines for resists of the invention include the following:

diazobicycloundecene;

diazabicyclononene;

di-butylethanolamine including di-tert-butylethanolamine;

dimethylundecylamine;

1,8-diazabicyclo[5.4.0]undec-7-ene;

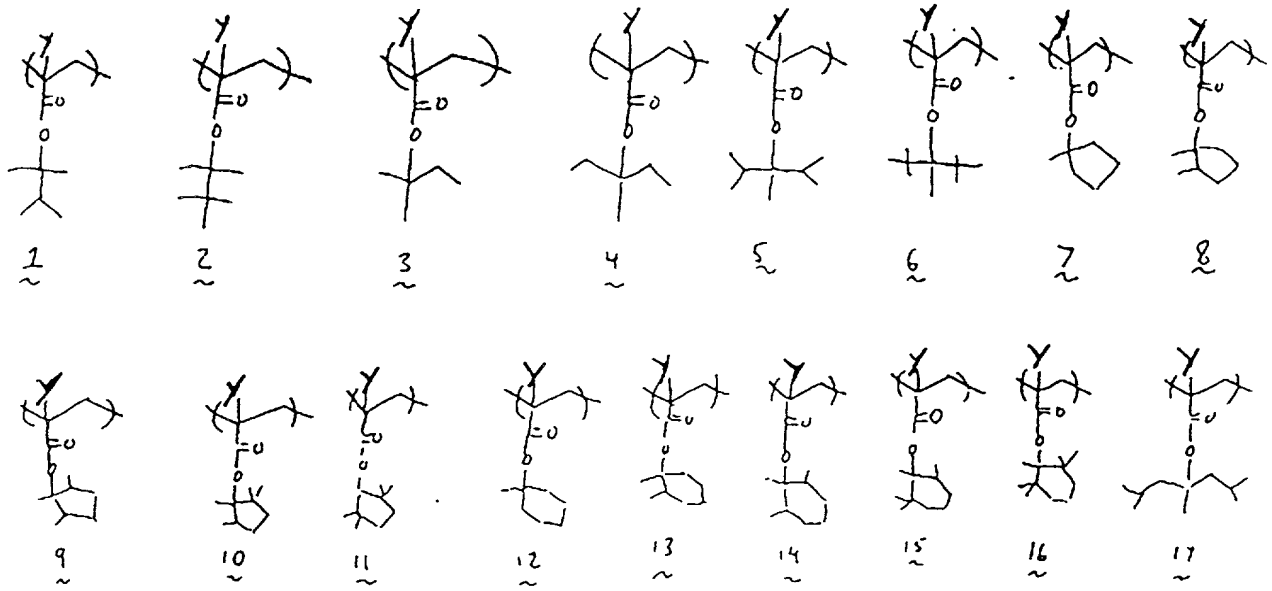
tri(propanol)amine including tri(isopropanol)amine;

sparteine;
N-ethyl dicyclohexyl amine;
pentrol;
tri-butylamine including tri-isobutylamine;
N,N-dibutyl-2-amino-ethanol;
and the like.

An added amine may be suitably used in a relatively wide range of amounts in a photoresist of the invention. For example, the added amine may suitably be present in amount of about 0.1 to 5 to 10 weight percent, based on total solids (all components except solvent) of a resist composition. Generally preferred is about 5 mole % of the added amine relative to theoretical amount of photoacid that can be generated by the PAG.

Preferred polymers for use as a resin binder have a deblocking monomer unit that can react with photogenerated acid. Suitable deblocking groups include pendant ester groups that can be provided e.g. by reaction of acrylate monomers. For example, suitable deblocking pendant ester groups include those of the Formula $-WC(=O)OR^5$, wherein W is a linker such as a chemical bond, an alkylene particularly C_{1-3} alkylene, or carbocyclic aryl such as phenyl, or aryloxy such as phenoxy, and R^5 is a suitable ester moiety such as an optionally substituted alkyl (including cycloalkyl) suitably having from 1 to about 20 carbons, more preferably about 4 to about 12 carbons; optionally substituted alkenyl (including cycloalkenyl) group suitably having from 2 to about 20 carbons, more preferably about 4 to about 12 carbons; optionally substituted alkynyl group suitably having from 2 to about 20 carbons, more preferably about 4 to about 12 carbons; optionally substituted alkoxy group suitably having from 1 to about 20 carbons, more preferably 2 to about 12 carbons; or a heteroalicyclic group that contains one or more N, O or S atoms and one or more rings having from 4 to about 8 ring members such as tetrahydrofuranyl, thienyl, tetrahydropyranyl, morpholino and the like. Specifically

preferred R^5 groups include e.g. t-butyl, tetrahydropyran, ethoxyethyl, or an alicyclic group including bridged groups such as such as adamantyl including 2-methyl-2-adamantyl, norbornyl, isobornyl and the like. Also preferred are polymers having ester repeat units of the above Formula where R^5 is a noncyclic or single ring alkyl group having 5 or more carbons and two or more secondary or tertiary carbon radicals, such as pendant esters of the following structures 1 through 17 (such polymers are also disclosed in copending U.S. application serial number 09/143,462, filed on August 28, 1998:



In each of the above structures 1 through 17, the substituent Y is preferably hydrogen or methyl, more preferably methyl.

Polymers for as a resin binder component also may have other units such as pendant cyano and itaconic anhydride groups. Preferably, the itaconic anhydride moiety

will be directly pendant to the polymer backbone, i.e. the moiety is directly pendant to a polymer bridge group without any alkylene, aryl or other group interposed between the polymer bridge group and the itaconic anhydride group. While the cyano group is preferably directly pendant to the polymer backbone, a linker group also may be interposed between the cyano group and a polymer bridge group.

Polymers used as resin binders of resists of the invention optionally may contain still further units such as groups that contribute to aqueous developability of a photoresist. For example, preferred polymer groups that contribute to aqueous developability contain carboxy or hydroxy moieties such as may be provided by condensation of acrylic acid, methacrylic acid, 2-hydroxyethyl methacrylate, or other monomers. Other optional polymer units include those that may be provided by condensation of a vinyl alicyclic group, e.g. 2-adamantyl-2-methyl methacrylate, isobornyl methacrylate and the like, or a non-cyclic alkyl group such as t-butyl methacrylate and the like.

Polymers of the invention can be prepared by a variety of methods. One suitable method is free radical polymerization, e.g., by reaction of selected monomers to provide the various units as discussed above in the presence of a radical initiator under an inert atmosphere (e.g., N_2 or argon) and at elevated temperatures such as about 70°C or greater, although reaction temperatures may vary depending on the reactivity of the particular reagents employed and the boiling point of the reaction solvent (if a solvent is employed). Suitable reaction solvents include e.g. tetrahydrofuran, dimethylformamide and the like. Suitable reaction temperatures for any particular system can be readily determined empirically by those skilled in the art based on the present disclosure. Monomers that can be reacted to provide a polymer of the invention can be readily identified by those skilled in the art based on the present disclosure. For example, suitable monomers include e.g. acrylonitrile, methacrylonitrile, allylcyanide, itaconic anhydride and the like. A variety of free radical initiators may be employed to prepare

the copolymers of the invention. For example, azo compounds may be employed such as azo-bis-2,4-dimethylpentanenitrile. Peroxides, peresters, peracids and persulfates also could be employed. See the examples which follow for synthesis and use of preferred resin binders.

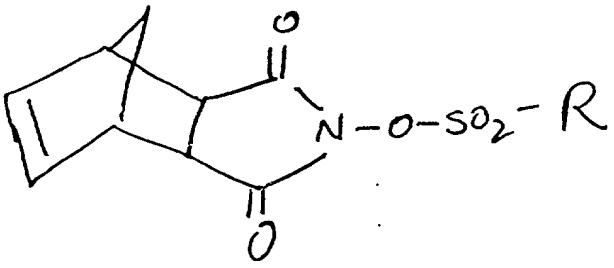
Preferably a polymer used as a resin binder component of a resist of the invention will have a weight average molecular weight (M_w) of 1,000 to about 100,000, more preferably about 2,000 to about 30,000, still more preferably from about 2,000 to 15,000 or 20,000, with a molecular weight distribution (M_w/M_n) of about 3 or less, more preferably a molecular weight distribution of about 2 or less. Molecular weights (either M_w or M_n) of the polymers of the invention are suitably determined by gel permeation chromatography.

As discussed above, the polymers of the invention are highly useful as a resin binder component in photoresist compositions, particularly chemically-amplified positive resists. Photoresists of the invention in general comprise a photoactive component and a resin binder component that comprises a polymer as described above.

The resin binder component should be used in an amount sufficient to render a coating layer of the resist developable with an aqueous alkaline developer.

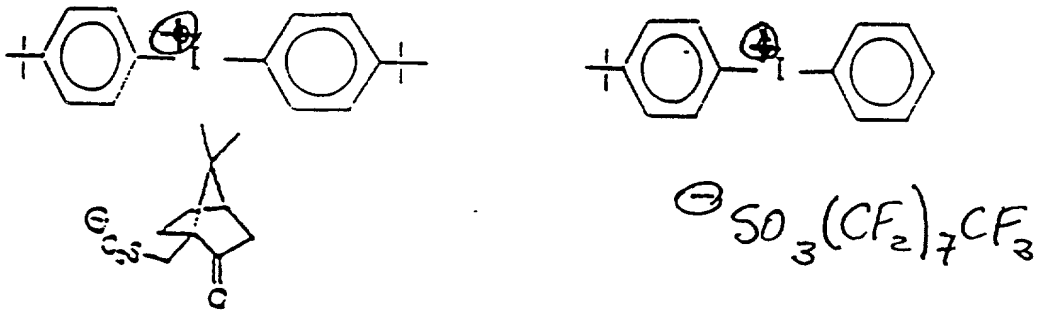
The resist compositions of the invention also comprise a photoacid generator (i.e. "PAG") that is suitably employed in an amount sufficient to generate a latent image in a coating layer of the resist upon exposure to activating radiation. As discussed above, preferred PAGs for use in resists of the invention are non-ionic compounds, although ionic PAGs such as onium salts also can be employed if desired.

One group of preferred PAGs for use in the resists of the invention include imidosulfonates such as compounds of the following formula:



wherein R is camphor, adamantane, alkyl (e.g. C_{1-12} alkyl) and perfluoroalkyl such as perfluoro(C_{1-12}alkyl), particularly perfluoro anions of perfluorooctanesulfonate, perfluorononanesulfonate and the like. A specifically preferred PAG is N-[(perfluorooctanesulfonyl)oxy]-5-norbornene-2,3-dicarboximide.

Sulfonate compounds are also may be employed such as sulfonate salts. Two suitable agents are the following PAGS 1 and 2:



1 2

Such sulfonate compounds can be prepared as disclosed in European Patent Application 96118111.2 (publication number 0783136), which details the synthesis of above PAG 1. Briefly, PAG 1 can be prepared by reaction of a mixture of potassium iodate, t-butylbenzene and acetic anhydride with sulfuric acid added dropwise to the mixture with ice-bath cooling. The reaction mixture is then stirred at room temperature for approximately 22 hours, water added with cooling to about 5-10°C and then washing with hexane. The aqueous solution of diaryliodium hydrogensulfate is then cooled to

about 5-10°C and then (+/-)-10-camphorsulfonic acid added followed by neutralization with ammonium hydroxide.

Also suitable are the above two iodonium compounds complexed with anions other than the above-depicted camphorsulfonate groups. In particular, preferred anions include those of the formula RSO_3^- where R is adamantane, alkyl (e.g. C_{1-12} alkyl) and perfluoroalkyl such as perfluoro (C_{1-12}alkyl), particularly perfluoro counter anions of perfluorooctanesulfonate, perfluorononanesulfonate and the like.

Other known PAGS also may be employed in the resists of the invention. For example, N-sulfonylocxyimides may be employed such as those described in International application WO94/10608, or non-ionic halogenated PAGs that generate a holgen acid (e.g. HBr) upon exposure to activating radiation as described e.g. in U.S. Patent 5,128,232 to Thackeray et al.

Photoresists of the invention also may contain other optional materials. For example, optional additives include anti-striation agents, plasticizers, speed enhancers, etc. Such optional additives typically will be present in minor concentrations in a photoresist composition except for fillers and dyes which may be present in relatively large concentrations, e.g., in amounts of from about 5 to 30 percent by weight of the total weight of a resist's dry components.

The compositions of the invention can be readily prepared by those skilled in the art. For example, a photoresist composition of the invention can be prepared by dissolving the components of the photoresist in a suitable solvent such as, for example, ethyl lactate, ethylene glycol monomethyl ether, ethylene glycol monomethyl ether acetate, propylene glycol monomethyl ether; propylene glycol monomethyl ether acetate and 3-ethoxyethyl propionate. Typically, the solids content of the composition varies between about 5 and 35 percent by weight of the total weight of the photoresist

composition. The resin binder and PAG components should be present in amounts sufficient to provide a film coating layer and formation of good quality latent and relief images. See the examples which follow for exemplary preferred amounts of resist components.

The compositions of the invention are used in accordance with generally known procedures. The liquid coating compositions of the invention are applied to a substrate such as by spinning, dipping, roller coating or other conventional coating technique. When spin coating, the solids content of the coating solution can be adjusted to provide a desired film thickness based upon the specific spinning equipment utilized, the viscosity of the solution, the speed of the spinner and the amount of time allowed for spinning.

The resist compositions of the invention are suitably applied to substrates conventionally used in processes involving coating with photoresists. For example, the composition may be applied over silicon wafers or silicon wafers coated with silicon dioxide for the production of microprocessors and other integrated circuit components. Aluminum-aluminum oxide, gallium arsenide, ceramic, quartz, copper, glass substrates and the like are also suitably employed.

Following coating of the photoresist onto a surface, it is dried by heating to remove the solvent until preferably the photoresist coating is tack free. Thereafter, it is imaged through a mask in conventional manner. The exposure is sufficient to effectively activate the photoactive component of the photoresist system to produce a patterned image in the resist coating layer and, more specifically, the exposure energy typically ranges from about 1 to 100 mJ/cm^2, dependent upon the exposure tool and the components of the photoresist composition.

Coating layers of the resist compositions of the invention are preferably photoactivated by a short exposure wavelength, particularly a sub-200 nm exposure wavelength. A particularly preferred exposure wavelength is about 193 nm.

Following exposure, the film layer of the composition is preferably baked at temperatures ranging from about 70°C to about 160°C. Thereafter, the film is developed. The exposed resist film is rendered positive working by employing a polar developer, preferably an aqueous based developer such as quaternary ammonium hydroxide solutions such as a tetra-alkyl ammonium hydroxide solution; various amine solutions preferably a 0.26 N tetramethylammonium hydroxide, such as ethyl amine, n-propyl amine, diethyl amine, di-n-propyl amine, triethyl amine, or methyldiethyl amine; alcohol amines such as diethanol amine or triethanol amine; cyclic amines such as pyrrole, pyridine, etc. In general, development is in accordance with procedures recognized in the art.

Following development of the photoresist coating over the substrate, the developed substrate may be selectively processed on those areas bared of resist, for example by chemically etching or plating substrate areas bared of resist in accordance with procedures known in the art. For the manufacture of microelectronic substrates, e.g., the manufacture of silicon dioxide wafers, suitable etchants include a gas etchant, e.g. a chlorine or fluorine-based etchant such a Cl_2 or CF_4/CHF_3 etchant applied as a plasma stream. After such processing, resist may be removed from the processed substrate using known stripping procedures.

All documents mentioned herein are incorporated herein by reference. The following non-limiting examples are illustrative of the invention.

Examples 1-19: Photoresist compositions of the invention

In Examples 1 -11, photoresist compositions were prepared by dissolving a combination of 0.2538 g of the photoacid generator perfluoro-octanesulphonate-norbonene dicarboximide (that photoacid generator referred to below as "POND" and was obtained from Daychem Corporation), and 3.365g of the resist polymer of Example 20 below into a solution containing an amount of the specified amine compound listed in Table 1 below (about 1.5×10^{-5} chemical equivalents of the amine compound), 0.0036 g of Silwet 7604 (Dow Corning Co., USA) and 21.375 g of propyleneglycol methyl ether acetate (Dow Corp., USA). The amine compounds were obtained from Aldrich Corporation. After dissolution, the resist composition was filtered through either a 0.1 μm or 0.2 μm Teflon filter into a clean bottle.

In Examples 12 - 19, photoresist compositions were prepared by dissolving a combination of 0.1813 g of perfluoro-octanesulphonate-norbonene dicarboximide (POND, obtained from Daychem Corporation), and 3.365g of the resist polymer of Example 20 below into a solution containing an amount of the specified amine compound listed in Table 1 below, 0.0036 g of Silwet 7604 (Dow Corning Co., USA) and 21.375 g of propyleneglycol methyl ether acetate (Dow Corp., USA). The amine compounds were obtained from Aldrich Corporation. After dissolution, the resist composition was filtered through either a 0.1 μm or 0.2 μm Teflon filter into a clean bottle.

Table 1

Photoresist compositions of Examples 1 through 19

Example No.	Amine Compound	Weight of Amine Added	Weight of POND added
1	THEDA	0.0044 g	0.2538 g
2	DMUDA	0.0030 g	0.2538 g
3	tri (nonafluro-n-butyl) amine	0.0101 g	0.2538 g
4	tri (isopropanol)amine	0.0029 g	0.2538 g
5	N,N,N',N'-tetraethylenediamine	0.0013 g	0.2538 g
6	sparteine	0.0018 g	0.2538 g
7	N-ethyl dicyclohexyl amine	0.0032 g	0.2538 g
8	pentrol	0.0020 g	0.2538 g
9	tri-isobutylamine	0.0028 g	0.2538 g
10	di-n-butyl N-ethanol amine	0.0026 g	0.2538 g
11	DBU	0.0023 g	0.2538 g
12	Proton Sponge	0.0023 g	0.1813 g
13	di-n-butyl N-ethanol amine	0.0023 g	0.1813 g
14	Coumarin 1	0.0023 g	0.1813 g
15	tri-n-octylamine	0.0023 g	0.1813 g
16	dimethylamino pyridine	0.0023 g	0.1813 g
17	tertra-n-butyl ammonium hydroxide	0.0023 g	0.1813 g
18	DBU	0.0023 g	0.1813 g
19	DABCO	0.0023 g	0.1813 g

In the above Table 1, THEDA = N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine; DMUDA = dimethylundecyl amine; DBU = 1,8-diazabicylco[5.4.0]undec-7-ene; DABCO = 1,4-diazabicyclo[2.2.2]octane

Example 20: Resist polymer synthesis

A photoresist binder polymer with a molar feed ratio of 31:22:10:14:23 of isobornyl methacrylate:tert-butyl methacrylate:methacrylic acid: methacrylonitrile: itaconic annhydride was prepared through the following procedure:

Into a 500 mL flask was placed 12.54 g of itaconic annhydride, 15.20 g of tert-butyl methacrylate, 4.58 g of methacrylonitrile, 4.28g of methacrylic acid, 33.57g of isobornyl methacrylate, and 100 mL of anhydrous tetrahydrofuran. All reagents were at least 99% pure. The flask was fitted with a magnetic stirring bar, a condenser and an addition funnel. All ingredients were sparged with N_2 gas for 20 minutes prior to reaction. In the condenser was placed 0.75 g of Vazo52 free-radical initiator and 25 mL of anhydrous tetrahydrofuran. The solution was brought to 70°C, and then the initiator was added over a 20 minute period. The flask was maintained at 70°C for 14 hours, and then cooled to room temperature. Polymer was obtained by precipitation into 3L of hexane, and dried in a Buchner funnel. Then the polymer was re-dissolved into 120 mL of acetone and reprecipitated into 3 L of hexane, and collected on a Buchner funnel. The polymer was dried overnight in a vacuum oven at room temperature. Yield was 49.96g

Examples 21-38: Lithographic Testing

The photoresist compositions of Examples 1-19 above were lithographically tested. To assess resolution capability, high-voltage cross-sectional scanning electron microscopic methods were used to examine the printed features. Minimal resolution in an imaged 1:1 pitch grating by choosing an exposure dose such that the patterned 1:1 160 nm lines and 160 nm spaces on the mask actually measured essentially 160nm in size respectively, and then determining the smallest, essentially full-thickness line which cleanly developed, had a flat top and did not leave residue on the substrate. Photospeed is the exposure dose required in forming such a pattern.

The lithographic processing was performed on modern wafer-processing tools (manufactured by FSI and SVG Companies) using both 150mm and 200mm silicon

wafers. All processing was done in an essentially base-contaminant free atmosphere (<5 ppb measure amines/ammonia). The wafers were coated with an organic ARC composition prior to subsequent processing. The photoresist was spun onto the wafers at about 3000 rpm and baked at 140°C for 60 seconds (PAB, post-apply bake) on a 150 μm proximity-gap plate and then rapidly cooled to room temperature to give a film thickness of 4200Å. Then the film was exposed using a resolution-test pattern on a ISI 0.60 NA ArF (193nm) wafer stepper at a partial coherence setting of 0.70. Immediately afterwards, the film was baked at 155°C for 60 seconds (PEB, post-exposure bake) on a 150 μm proximity-gap plate, and then rapidly cooled to room temperature. Immediately afterwards the film was developed using a 60 second track-single-puddle process with 0.26 N tetramethylammonium hydroxide developer. Lithographic results are detailed in Table 2 below.

Table 2

Results from lithographic testing (Examples 21-38) of Photoresist Compositions of Examples 1-19 respectively.

Example	Composition of Example	Es	ResL	Comments
21	1	>45	0.16	slow photospeed
22	2	34	0.14	good results
23	3	<15	ND	poor adhesion and resolution
24	4	34	0.14	good results
25	5	36	0.15	fair performance
26	6	36	0.14	good results
27	7	38	0.14	good results
28	8	24	0.14	rough sidewalls
29	9	22	0.14	good results
30	10	34	0.14	good results
31	11	34	0.14	good results

Table 2 - continued

32	12	50	0.15	resist composition turns yellow color
33	13	52	0.15	good results
34	14	52	0.18	resist lines "crack" and peel
35	16	60	0.17	resist lines break and become wavy
36	17	ND	ND	gross adhesion failure, composition decomposes
37	18	52	0.15	good results
38	19	ca. 70	0.17	granular appearance

In Table 2 above, ResL refers to the resolution at Es. Es is in units of mJ/cm^2 and ResL is in units of nm. ND indicates that the specified parameter could not be determined because of resist failure or other poor performance.

As the results indicate in Table 2 above, amine additives of the invention exhibit excellent lithographic results at 193 nm imaging, particularly with respect to the comparison (non-invention) amine additives.

More specifically, Examples 22, 24, 26-27, 29-31, 33 and 37 use resist compositions containing amine additives of the invention. These examples showed good resolution, namely 0.14 micron patterns, with good pattern fidelity. These compositions display imaging results which are suitable for advanced lithographic processing.

Examples 23, 25, 28, 32, 34-36 and 38 use compositions which include amines which are not part of preferred aspects of the invention. Lithographic results with these examples showed poor pattern fidelity, adhesion failure and evidence of decomposition in solution.

Examples 32 and 36 use compositions which include additives of Proton Sponge and tetramethylammonium hydroxide, respectively, both of which have been reported to yield reasonably good results. It has been found those additives can provide reasonably good results when formulated for use in a composition containing a poly(4-vinylphenol) polymer, and ionic PAG and exposed using 248 nm radiation. However, unexpectedly, when used in a composition which contained a non-aromatic polymer and a non-ionic PAG, those additives gave poor results.

Similarly, it has been found that Coumarin 1 can provide reasonably good results when formulated for use in a composition containing a poly(4-vinylphenol) polymer, and ionic PAG and exposed using 248 nm radiation. However, unexpectedly, when used in a resist composition which contained a non-aromatic polymer and a non-ionic base, that additive gave poor results. See the results of Example 34 above.

The foregoing description of the invention is merely illustrative thereof, and it is understood that variations and modification can be made without departing from the spirit or scope of the invention as set forth in the following claims.

What is claimed is:

1. A photoresist composition comprising a resin binder, a photoacid generator compound and a non-aromatic amine compound that has from about 7 to about 20 carbon atoms and contains no primary or secondary amine groups.

2. A photoresist of claim 1 wherein the amine compound has from about 9 to about 16 carbon atoms.

3. A photoresist of claim 1 wherein the amine compound does not contain two tertiary amine groups linked by an optionally substituted ethylene group.

4. A photoresist of claim 1 wherein the amine compound is
diazobicycloundecene;
diazabicyclononene;
di-butylethanolamine;
dimethylundecylamine;
1,8-diazabicyclo[5.4.0]undec-7-ene;
tri(propanol)amine;
sparteine;
N-ethyl dicyclohexyl amine;
pentrol;
tri-butylamine; or
di-butyl-N-ethanol amine.

5. A photoresist of claim 1 wherein the photoacid generator is a non-ionic compound.

6. A photoresist of claim 1 wherein the resin binder comprises a polymer that contains pendant photoacid labile moieties and is substantially free of any aromatic groups.

7. A photoresist of claim 1 wherein the resin binder is completely free of any aromatic groups.

8. A positive-acting photoresist composition comprising 1) a resin binder that comprises a polymer that contains pendant photoacid labile moieties and is substantially free of any aromatic groups, 2) a non-ionic photoacid generator compound, and 3) a non-aromatic amine compound that has from 9 to 16 carbon atoms and contains no primary or secondary amine groups, and wherein the amine does not contain two tertiary amine groups linked by an optionally substituted ethylene group .

9. A method of forming a positive photoresist relief image, comprising:

(a) applying a coating layer of a photoresist of claim 1 on a substrate; and

(b) exposing and developing the photoresist layer to yield a relief image.

10. The method of claim 9 wherein the photoresist layer is exposed with radiation having a wavelength of about 193 nm.

11. An article of manufacture comprising a microelectronic wafer substrate or flat panel display substrate having coated thereon a layer of the photoresist composition of claim 1.

12. A photoresist composition comprising a resin binder, a photoacid generator compound and a non-aromatic amine compound that comprises either 1) a tertiary nitrogen alicyclic ring member; or 2) a tertiary nitrogen that is not a ring member, and is substituted by at least two secondary or tertiary carbon radicals.

13. A photoresist of claim 12 wherein the amine compound comprises a tertiary nitrogen alicyclic ring member.

14. A photoresist of claim 12 wherein the tertiary nitrogen ring member is at a junction position of at least two rings of a multiple ring compound.

15. A photoresist of claim12 wherein the amine compound is a bicyclic compound.

16. A photoresist of claim 12 wherein the tertiary nitrogen radical is substituted by two tertiary carbon radicals and contains from about 6 to about 24 non-hydrogen atoms.

17. A photoresist of claim 12 wherein the photoacid generator is a non-ionic compound.

18. The photoresist of claim 12 wherein the resin binder comprises a polymer that contains pendant photoacid labile moieties and is substantially free of any aromatic groups.

19. A method of forming a positive photoresist relief image, comprising:

(a) applying a coating layer of a photoresist of claim 12 on a substrate; and

(b) exposing and developing the photoresist layer to yield a relief image.

20. The method of claim 19 wherein the photoresist layer is exposed with radiation having a wavelength of about 193 nm.

21. An article of manufacture comprising a microelectronic wafer substrate or flat panel display substrate having coated thereon a layer of the photoresist composition of claim 11.

ABSTRACT

The present invention provides novel photoresist compositions that comprise a resin binder, a photoacid generator compound and an added amine component. In a first aspect, the added amine preferably is 1) non-aromatic 2) has from about 9 to about 16 carbon atoms, 3) contains no primary or secondary amine groups, and/or 4) contains no multiple tertiary amine groups where two tertiary groups are separated by a linkage of optionally substituted ethylene. In a related aspect, the added amine is a non-aromatic amine that comprises either 1) a tertiary nitrogen alicyclic ring member, and preferably is at junction position between a bicyclic or other multi-ring ring system; or 2) a tertiary nitrogen that is not a ring member, and is substituted by at least two tertiary or quaternary carbon radicals.

Docket No.
50351

Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

PHOTORESIST COMPOSITIONS PARTICULARLY SUITABLE FOR SHORT WAVELENGTH IMAGING

the specification of which

(check one)

☒ is attached hereto.

☐ was filed on _____ as United States Application No. or PCT International Application Number _____

and was amended on _____
(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)			Priority Not Claimed
_____ (Number)	_____ (Country)	_____ (Day/Month/Year Filed)	☐
_____ (Number)	_____ (Country)	_____ (Day/Month/Year Filed)	☐
_____ (Number)	_____ (Country)	_____ (Day/Month/Year Filed)	☐

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

(Application Serial No.)	(Filing Date)
(Application Serial No.)	(Filing Date)
(Application Serial No.)	(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. *(list name and registration number)*

Peter F. Corless (Reg. No. 33,860)
Sewall P. Bronstein (Reg. No. 16,919)
David G. Conlin (Reg. No. 27,026)
George W. Neuner (Reg. No. 26,964)
Ernest V. Linek (Reg. No. 29,822)
Linda M. Buckley (Reg, No. 31,003)
Ronald I. Eisenstein (Reg. No. 30,628)
Peter J. Manus (Reg. No. 26,766)
David S. Resnick (Reg. No. 34,235)
John L. Welch (Reg. No. 28,129)
Cara Z. Lowen (Reg. No. 38,227)
William J. Daley, Jr. (Reg. No. 35,487)
David D. Lowry (Reg. No. 38,538)
Robert L. Buchanan (Reg. No. 40,927)
Christine C. O'Day (Reg. No. 38,256)

Robert L. Goldberg (Reg. No. 22,456)

Send Correspondence to:

Peter F. Corless, Esq.
P.O. Box 556
Marlborough, MA 01752

Direct Telephone Calls to: *(name and telephone number)*

Peter F. Corless, Esq. (508)485-7772

Full name of sole or first inventor

Peter Trefonas, III

Sole or first inventor's signature: Peter Trefonas

Date: December 22 1998

Residence

40 Summerhill Road, Medway, Massachusetts 02053

Citizenship

United States

Post Office Address

Same

Full name of second inventor, if any

Gary N. Taylor

Second inventor's signature: Gary N. Taylor

Date: Dec. 22, 1998

Residence

35 Smith Road, Northboro, Massachusetts 01532-1051

Citizenship

United States

Post Office Address

Same